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Conversion of biorenewable feedstocks: New challenges in heterogeneous catalysis

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Conversion of Biorenewable Feedstocks: New Challenges in Heterogeneous Catalysis

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For biorenewable feedstocks to serve as a significant source of chemicals and/or fuels, the development of new chemical processes as well as biological processes will be required. However, the conversion of biorenewable feedstocks with heterogeneous catalyst-based processes provides new challenges in inorganic catalyst research and development relative to historical work with petrochemical feedstocks. These catalyst and process challenges include the need to convert highly functionalized molecules with high selectivity, to develop stable catalytic liquid−solid interfaces in which the liquid phase is commonly aqueous, to control solvent phase effects and to develop novel reaction systems. While some of these challenges will be addressed using novel catalytic materials, others will need to be overcome through design of new catalytic reaction systems. Examples of emerging research results demonstrating unique approaches that have been taken to begin to address the efficient conversion of biorenewable feedstocks to chemicals and fuels are discussed.

Introduction

As sustainability becomes an increasingly important expectation for chemical and petroleum companies, the utilization of renewable carbon is receiving rapidly expanding attention. To be a renewable carbon source, a carbon-based feedstock must be generated on the same time scale in which it is used and as such, a key resource for renewable carbon will undoubtedly be biomass. As the chemical and petroleum industry begins to turn its attention to alternative sources of raw materials derived from biomass, the concept of a biorefinery producing chemicals, fuel, and power from renewable raw materials is now well-recognized as an important approach. To be successful, catalytic processes will need to be developed for the biorefinery to parallel the chemical refinery in terms of process cost, efficiency, and environmental impact.

Despite the fact that heterogeneous catalysis has been a key enabling technology in the chemical and petroleum industries, the use of heterogeneous catalysts in existing biorefineries, e.g., corn wet mills and wood processing plants, is quite limited. Due to the higher level of functionality present in biomass-based feedstocks, heterogeneous catalyst technologies developed for the petrochemical industry are typically inadequate for selectively converting biomass to chemicals and fuels. Further complicating the conversion of biomass is the requirement that the reactions will typically need to be accomplished in the condensed phase, where the solvent is commonly water, rather than the gas phase used for petrochemicals. For these reasons new catalyst technology approaches will be needed for converting biomass to useful products. The constraints imposed by biorenewable conversions have led to significant interest in using biocatalysts. While important progress continues to be made with biocatalysts, significant technical challenges around catalyst robustness for large-scale application still remain. If biorenewables are to become a significant source of fuels and industrial chemicals, both chemical catalyst and biocatalyst technologies will need to be developed.

Despite the integral role of catalysis to the biorefinery, the fact remains that limited fundamental information is known about heterogeneous catalyst use for the conversion of biorefinery building blocks. Modern catalytic processes have been tailored for hydrocarbon feedstocks with scant attention paid to the chemical features inherent in biomass and its derivatives. Catalyst technology has been extensively developed for olefin conversions, e.g., selective hydrogenation, selective oxidation, isomerization, reforming, etc., such that the best metal catalysts to achieve a specific class of conversions have been identified and the underlying mechanisms around olefin transformation chemistry are largely elucidated. Therefore, the catalytic conversion of these substrates with low-level functionalization is well developed. As petrochemical companies extend catalyst research, a prime target has been the activation of alkanes, which corresponds to converting a substrate with even less functionalization. The catalytic conversion of biomass and its derivatives pushes in the opposite direction with the need to achieve transformations in the presence of a high degree of substrate functionality. The high level of functionality will generally impose a new processing restriction as well. Unlike with alkenes and alkanes that are predominantly processed in the gas phase, biomass-derived materials will likely need to be processed in the condensed phase with water commonly as the solvent.

The catalytic conversion of biomass-derived materials in the aqueous phase introduces a broad array of new questions ranging from those concerning fundamental mechanisms to process applications. How do molecules with a high level of functionality adsorb on metal or metal oxide surfaces? How can specific C−C or C−O bonds be converted in the presence of multiple reactive functional groups? What role will water play in the reactions? How must catalytic structures be modified for biomass? How can hydrothermal stability be built into the catalysts? Can the reaction systems be coupled with separations? The answers to these questions will be an important bridge to solving the product-specific catalysis technology challenges for biomass utilization.

Adsorption of Carbohydrates on Metals/Metal Oxides

Whereas the adsorption of alkenes on metals and metal oxides has been extensively examined, understanding of the adsorption behavior of carbohydrates and their derivatives, which have multiple functional groups through which adsorption can occur, is quite limited. The challenge associated with understanding

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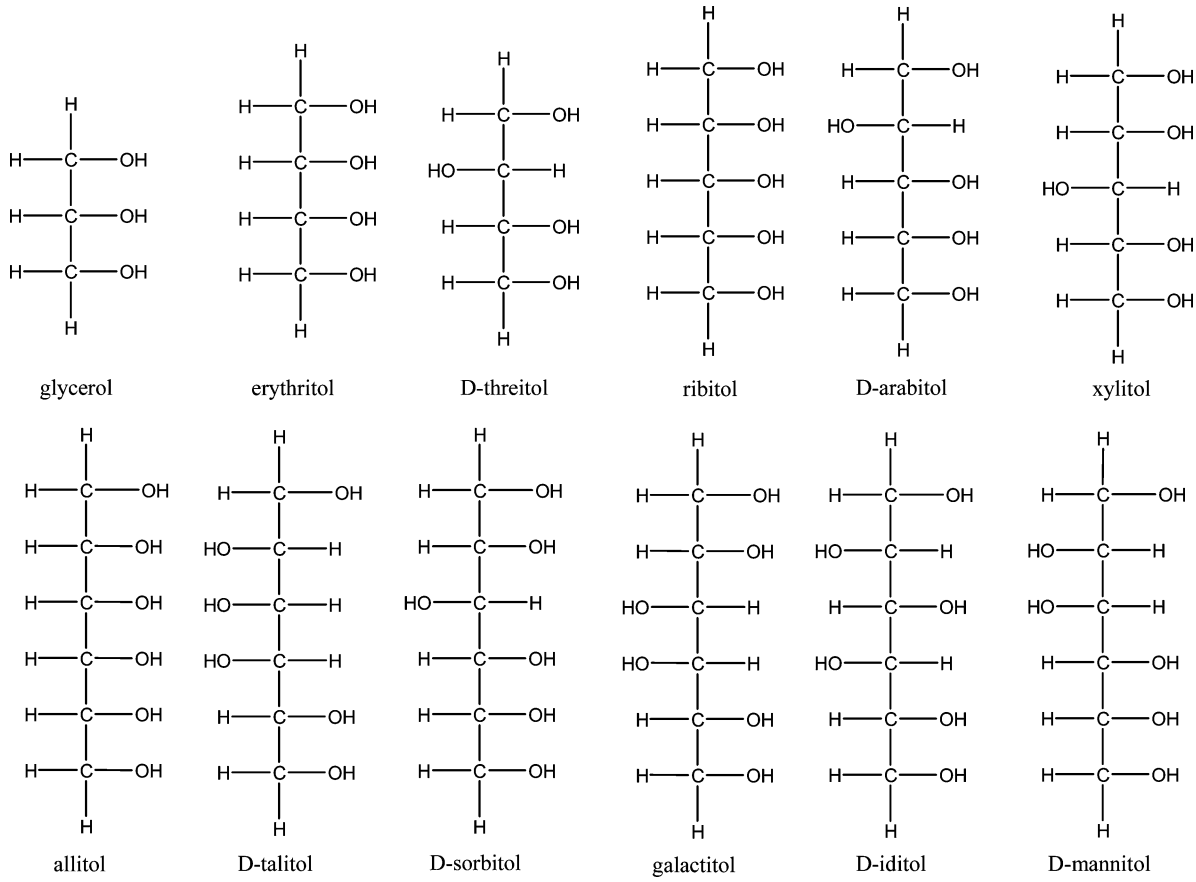

Figure 1. Fischer Projections of the C3−C6 higher polyols.

adsorption behavior of these multifunctional group molecules is even more complex when trying to characterize adsorption under reaction conditions, as the reaction will commonly be performed in the condensed phase. Additionally, carbohydrates and their derivatives have stereoisomers that can have very different adsorption behavior.

As an example, the adsorption of a range of sugars in the aqueous phase onto hydrous zirconium oxide and iron oxide was examined using a Langmuir monolayer adsorption isotherm approach.[1] Aldohexoses, aldopentoses, and ketohexoses as well as several derivatives of these sugars were used in the testing. The experimentally determined Langmuir equilibrium constant and maximum amount of the sugar required to form a monolayer on the surface were strongly dependent on the stereoisomer used. For example, the Langmuir equilibrium constant found for D-ribose was five times that for D-glucose and the maximum amount of D-ribosee in a monolayer was 50% higher. In general, it was found that the stereochemistry of the three neighboring hydroxyl groups on the C(2), C(3), C(4) carbon atoms in aldohexoses or the C(2), C(3), C(4) carbon atoms in ketohexoses strongly impacted the resulting adsorption behavior. The differences in the Langmuir isotherm adsorption behavior were significantly more pronounced for the interaction of the sugars with hydrous zirconium oxide than with hydrous iron oxide. It was speculated that the difference between the two hydrous metal oxides could be attributed to the ionic radii of the metal ions.

The difference in the adsorption behavior of stereoisomers of higher polyols, which are hydrogenated forms of the sugars, was examined indirectly through their relative initial reactivity under hydrogenolysis conditions.[2] The relative rate of disappearance of higher polyols was compared using a Ru on carbon catalyst at 205 and 240 °C in the presence of 100 bar of hydrogen.[2] The Fischer Projections of the C3−C6 higher polyols are shown in Figure 1 and the initial hydrogenolysis rates for those having solubility in water are given Table 1. As can be seen from these data, the reaction rates were not correlated with the carbon number, as stereoisomers had different reactivities. One could speculate that these differences in initial rates could be at least partially attributed to the adsorption characteristics of the different stereoisomers.

Table 1. Initial Reaction Rates for a Variety of Polyols over a Ru/C Catalyst (0.5 M Polyol Concentration, 100 bar H_2, and pH Adjusted to 11.5 Using CaO)

compound	reaction rate (205 °C mmol/min)	reaction rate (240 °C mmol/min)
glycerol	3.9	10.3
erythritol	3.4	10.1
threitol	2.0	5.0
ribitol	3.3	11.0
arabitol	3.0	9.5
xylitol	2.5	6.4
mannitol	2.8	7.8
sorbitol	2.5	6.7
galactitol	N/A	3.5

The fact that stereoisomers of carbohydrates and their derivatives have distinctly different adsorption characteristics only addresses initial adsorption of the reactant molecule. Reaction products that also possess significant functionalization will create the need to understand competitive adsorption. Several studies with glycerol, ethylene glycol, and propylene glycol found that all readily adsorb on Ru, but when present

together glycerol and ethylene glycol are preferentially adsorbed relative to propylene glycol.[3,4]

Selective Bond Cleavage

Biorenewable feedstocks will typically consist of multiple functional groups with the most common for carbohydrate-based feedstocks being hydroxyl groups. As these feedstocks generally contain excess oxygen for fuel or chemical applications, there is a need to develop conversion technology that will selectively remove oxygen. Reactions of particular interest to accomplish oxygen removal are dehydration and decarbonylation/decarboxylation, although when the goal is to produce fuels, oxygen removal can also be achieved during condensation or ketonization reactions.[5−11]

In the dehydration of polyhydroxylated compounds, the goal is to control C−O cleavage without concomitant C−C cleavage. A reaction that clearly demonstrates these competing challenges is the hydrogenolysis of sorbitol, xylitol, or glycerol.[12−16] This reaction is thought to be initiated by dehydrogenation of the sugar alcohol to either an aldehyde or ketone, so a kinetic mechanism for the system must address the relative reactivity at the different carbon positions as well as the adsorption behavior of the reactant. The range of reaction considerations in the hydrogenolysis reaction nicely represents the types of issues that are present in the catalytic conversion of many carbohydrate-derived species and can be used to develop insight into the ability to selectively break C−C and C−O at specific locations.

The reaction sequence that has been postulated for the hydrogenolysis of sugar alcohols is dehydrogenation of the alcohol to an aldehyde or ketone, which can subsequently undergo C−O cleavage through a dehydration reaction, C−C cleavage through a retro-aldol reaction, or rehydrogenation to the starting sugar alcohol.[17−19] The postulated mechanisms for the dehydration and retro-aldol reactions are shown in Figure 2 for glycerol. The catalyst system most frequently used for the reaction is Ru/carbon in a highly basic solution. In this previously proposed reaction sequence, the dehydrogenation/hydrogenation reactions are metal catalyzed and the dehydration/retrol-aldol reactions by solution hydroxyls. In more recent work with glycerol hydrogenolysis, the metal function has been found to play a role in the cascade of reactions leading to its dehydration to propylene glycol.[4,20,21] Additionally, results from hydrogenolysis of C5 sugar alcohols suggest the C−C cleavage can potentially occur through decarboxylation as well as the retro-aldol reaction.[2]

An additional level of complexity imparted by the conversion of C4 and higher sugar alcohols is that they can exist as different stereoisomers, as shown in Figure 1. While hemicellulose from biomass will largely consist of xylose with some arabinose, comparison of the hydrogenolysis reactivity of the three C5 sugar alcohol stereoisomers demonstrated the complexity of the aqueous-phase conversion for these species. Not only did the C5 sugar alcohols have different reactivities as shown in Table 1, they also had very different product selectivities. These differences in reaction product selectivities demonstrated that the reactivity of the hydroxyl groups at the carbon positions along the molecules were not equal. It has been shown that the product selectivity could be further modified with the Ru/C catalyst when sulfur was introduced to the reaction system. For example, introduction of sulfur into the glycerol hydrogenolysis reaction system increased the selectivity to propylene glycol relative to ethylene glycol and into the xylitol reaction system it suppressed the formation of C4 sugar alcohols.[2,17,21]

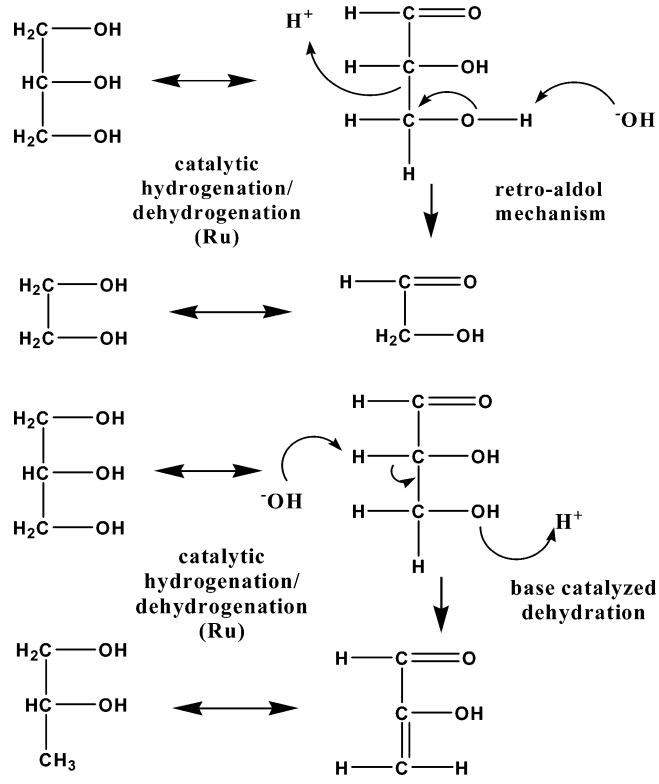

Figure 2. Proposed retro-aldol and dehydration reactions in the hydrogenolysis of glycerol.

Despite the extensive work on sugar alcohol hydrogenolysis, which has culminated in companies publicly announcing propylene glycol production from either glycerol or sorbitol, the complex reactivity of the polyhydric alcohols has not been definitively elucidated. The understanding of selective C−O cleavage remains an important research challenge.

Aqueous Phase Considerations

Carbohydrates and their multifunctional derivatives commonly have limited or no volatility and as such their conversion systems are likely to use the condensed phase. As the deconstruction of starch or cellulose to monosaccharides is performed in water, subsequent condensed phase processing will likely be in the aqueous phase. Heterogeneous catalysts have received relatively little attention with respect to how the presence of condensed water at the catalyst/solution interface can influence the kinetics and mechanisms of the resulting reactions.

Results from Neurock and co-workers demonstrated the new considerations introduced by the presence of the catalyst/solution interface in the reaction system. They used *ab initio* molecular dynamics to examine a number of aqueous phase catalytic reaction systems including the dissociation of acetic acid over Pd,[22] the hydrogenation of formaldehyde over Pd,[23] and the oxidation of CO to CO_2 over Pt/Ru.[24,25] Their simulations included the metal surface and adsorbates as well as a large ensemble of water molecules. The presence of the aqueous solution phase was found to change the thermodynamics and kinetics for many of the elementary reaction steps including adsorption, diffusion, desorption, and surface reactions. The reaction steps that involve charge transfer were most strongly impacted. While they found the expected effects of water solvation, they also found the solution could play an important role in the reaction mechanism through direct participation in the catalytic pathways.

An interesting example from their work was analysis of the possible hydrogenation pathways involved in the Pd-catalyzed hydrogenation of formaldehyde.[23] This system serves as a nice model for the hydrogenation of the aldehyde groups that could be required in the conversion of carbohydrate-derived species. They found the presence of the aqueous media reduced the hydrogenation activation barrier for either the carbon or the oxygen end of the molecule. Particularly intriguing is that they found a new energetically favorable pathway enabled by the aqueous phase. The pathway involved a surface hydrogen atom transferring an electron to the surface and then migrating into solution as a proton where the water phase network of local hydrogen bonds facilitated its movement to the active site where it hydrogenated the surface intermediate. For this new pathway, the metal both bonded the adsorbate to the surface and assisted in charge transfer. The charge transfer, which facilitated the electron release from the surface hydrogen creating a proton in solution, was able to occur because the Pd had a high enough work function to accept an electron.

Computational studies on the dissociation of acetic acid over Pd in an aqueous media also demonstrated the possibility of an altered reaction mechanism.[22] In the gas phase over Pd, the homolytic dissociation of acetic acid was found to be the most energetically favorable pathway. However, upon introduction of an aqueous phase the possibility of a heterolytic dissociation into an acetate ion and proton was found to be energetically possible.

The important aspect suggested by these modeling results is that the aqueous phase can not only influence the thermodynamics and kinetics of the reaction system, but can actually change the pathway by which the catalytic reaction occurs.

Catalyst Design for Biomass Conversion

Given that biorenewable-derived molecules will commonly need to be converted in the condensed phase, designing catalysts for converting these molecules will not only need to consider the chemistry at the active site, but also the reaction sphere around the active site. Enzymes have evolved to create these active domains in which the active site itself can consist of multiple amino acid moieties and the amino acids surrounding the active site can modify the reaction sphere around the active site. Taking this cue from nature, heterogeneous catalysts in which both the active site and reaction sphere are carefully controlled may prove to be particularly effective in the active and selective conversion of biorenewables.

Diaz et al.[26−30] examined the use of acid-functionalized mesoporous silicas to control the reaction environment in the catalytic esterification of glycerol with fatty acids to produce monoglycerides. Although glycerol esterification with fatty acids can lead to formation of mono-, di-, or triglycerides, only the chemical properties of the monoglycerides are suitable as an emulsifying agent and so there is a need to minimize the formation of di- and triglycerides. In constructing their catalysts, they used three attributes within the mesopores to control the catalytic performance of the material. First propylsulfonic acid groups were tethered to the interior of the pore. This functionalization was performed on mesoporous materials, which all had narrow pore distributions but with different average pore diameters. The use of the strong acid group in conjunction with tuning the pore diameter led to a MCM-41-SO_3H catalyst having high activity and selectivity for glycerol esterification to monoglycerides. The good catalytic performance of propylsulfonic acid-functionalized mesoporous silica catalyst was attributed to a combination of strong acidic sites located insides the mesopores as well as the narrow pore size distribution that diminished the formation of secondary di- and triglyceride products. The catalytic activity of the propylsulfonic acid-functionalized mesoporous silica catalyst was compared to that of *p*-toluenesulfonic acid (pTSA), which had high activity but poor selectivity to the desired monosaccahrides. A third attribute that was examined was the introduction of a second organic group by functionalizing MCM-41 materials with both alkyl groups and propylsulfonic acid groups. They found that the esterification reaction rate was improved with an increase in alkyl group loading, which suggested that water had been excluded from the reaction environment within the pore. The methylated propylsulfonic acid-functionalized MCM-41 catalyst had a 3-fold increase in catalytic activity relative to the nonmethylated organosulfonic acid-functionalized mesoporous silica material.

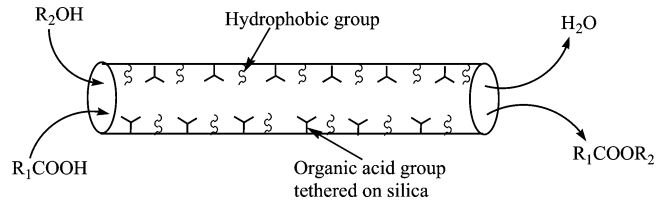

Figure 3. Schematic of mesoporous silica functionalized with organosulfonic acid and hydrophobic groups for fatty acid esterification with alcohol.[32]

Mesoporous scaffolds offer the opportunity to control the reaction environment around an active site by controlling the placement of functional groups in and on the scaffold materials. Controlled placement of functional groups in mesoporous silicas was examined with the resulting catalysts tested in the esterification of fatty acids with short-chain alcohols.[31−33] As water is a product of this reversible reaction, a synthesis strategy was used that created an environment in which water was excluded from the mesopores by introducing hydrophobic groups into the mesopores of the organosulfonic acid-functionalized mesoporous silica catalyst as shown schematically in Figure 3.[31,32] Two methods were used to integrate hydrophobic groups into propylsulfonic acid-functionalized mesoporous silica through either grafting on the preformed surface of the propylsulfonic acid-functionalized hybrid material or by co-condensation with the propylsulfonic acid and silica precursors. The mesoporous silica catalyst that was synthesized by the co-condensation technique, which placed the hydrophobic groups within the pores, gave significantly higher catalytic performance than the catalyst without hydrophobic group incorporation and the grafted catalyst, which would preferentially place the hydrophobic groups on the particle surfaces and near the pore mouths. It was also shown that the location of the propylsulfonic acid groups within the mesoporous materials could alter the acidity of the resulting material, as intentionally placing the sulfonic acid groups in close proximity through the use of a disulfide precursor decreased the pK_a value relative to the same number acidic sites incorporated using a propyl thiol precursor.[32]

The examples discussed above concerning control of the reaction sphere around the catalytic site had only low levels of water in the condensed phase. When water is the predominant phase, the ability to control the reaction sphere is even more difficult. With a Brønsted acid catalyst, the dissociated proton is relatively mobile and can exist at a molecularly significant distance from its anion pair due to the charge shielding capability of water. Given this proton mobility, new catalyst design

strategies have to be developed if there is a desire to control the reaction sphere around a specific active site.

Hydrothermally Stable Catalytic Materials

The presence of a condensed phase in a reaction system creates a new challenge involving finding catalysts that possess adequate stability. The challenge can be magnified when the reaction is being performed in the aqueous phase. Hydrothermal stability has been a longstanding issue for heterogeneous catalysts, which has received a great deal of attention. However, much of the work on creating hydrothermally stable solid catalysts has focused on recalcitrance to water vapor and not condensed water. Aqueous-phase catalytic conversions of biorenewables will necessitate solid catalysts that can maintain their stability to temperatures as high as 230 °C.

An interesting class of materials that has been examined for use in the conversion of biorenewable molecules is sulfonated carbons. Using glucose carbonization followed by sulfonation with concentrated sulfuric acid, sulfonated carbons were produced.[33,34] Depending on the carbonization conditions, carbon-based materials with acid content of up to 1.34 mmol/g were reported. It was speculated that the carbonized glucose formed polycyclic aromatic sheets with the sulfonic acid groups bound to the edges of the sheets.[34] The sulfonated carbon materials were found to have good activity for fatty acid esterification with methanol and were stable to repeated batch reaction testing at temperatures of 80−180 °C. The stability of sulfonated carbons in aqueous media was tested using the cellulose hydrolysis reaction at 150 °C.[35] In this case, the sulfonated carbon catalysts were synthesized by sulfonating activated carbon. The catalyst was found to maintain its activity through three hydrolysis cycles, but it should be noted that the number of sulfonic acid groups was not measured at the end of the three cycles to determine whether sulfur loss had occurred.

Although using sulfonated carbonized glucose appeared to yield a catalyst that had good stability in condensed phase reactions, these materials did not provide a means for controlling the pore size distribution of the catalysts. Therefore, several approaches have been taken to create mesoporous sulfonated carbons with narrow pore size distribution. In one approach, sucrose was impregnated into SBA-15 and then carbonized.[36] Following silicon removal by washing with HF, the resulting mesoporous carbon was sulfonated. The carbon-based catalytic material was found to be stable in multiple reaction cycles for liquid-phase Beckmann rearrangement of cyclohexanone oxime. A similar approach was used to make sulfonated carbon−silica mesoporous composites in which the silica was not removed.[37] The MCM-48-based composite materials were found to maintain their ordered mesoporous structure upon being exposed to boiling water for 48 h. The mesoporous structure of MCM-48 when not coated with carbon collapsed within 3 h in boiling water. The composite material was found to be an active esterification catalyst.

While these sulfonated carbon materials appear to have promising hydrothermal stability properties, key characterization validating the long-term stability of the materials has not been reported. Reproducible activity through 3−5 batch reaction cycles, although important, is inadequate to determine whether the sulfonic acid groups are slowly being lost. Also, acid-catalyzed biorenewable reactions can require that the catalysts be stable in the aqueous phase at temperatures as high as 230 °C, so the sulfonated carbon materials need to be tested at temperatures above boiling water to determine their potential range of application.

Novel Reaction Systems

As biorenewable conversions reaction systems will commonly involve a condensed phase, an important challenge is separating the desired product from the reaction medium. Appropriate selection of the catalyst and reaction system can facilitate this separation, so it is useful to include separation considerations when developing a catalytic reaction system for biorenewable feedstocks. While the goal of integrating separation considerations with the reaction system typically involves producing a product that is more easily removed from the reaction medium, another objective can be to enhance product selectivity. The multifunctional nature of biorenewable-derived molecules makes selective conversion to a desired product more difficult since the product will often have significant reactivity as well. Therefore, removal of the product from the reaction medium can have the advantage of improved selectivity.

Dumesic and co-workers have described the conversion of aqueous-phase carbohydrates to monofunctional hydrocarbons (alcohols, ketones, heterocyclics, and acids) using a Pt−Re catalyst.[7,38] The C4 and higher monfunctional species that were produced formed an organic phase that was immiscible with the aqueous phase. With a 60 wt. % solution of sorbitol in water, they were able to recover as much as 60 mol % of the original carbon in the feedstock within an organic phase when the reaction system was operated at 230 °C, 27 bar, and space velocity of 1.2 h^{-1}.[7] By operating their system at conditions leading to monofunctional hydrocarbons, a simple separation of the product was possible. The monofunctional hydrocarbons could then be upgraded to fuels through aldol condensation and ketonization C−C coupling reactions to produce fuels.[5−11]

The goal of incorporating separation considerations into the reaction system was also accomplished in the biphasic production of hydroxymethylfurfural (HMF) from fructose.[39−41] In this system, the reactive aqueous phase in the biphasic reactor contained an acid catalyst and the fructose feedstock, and the extracting phase contained a low miscibility organic solvent that served to continuously extract the HMF product. The extraction of the HMF to the nonreactive organic phase greatly reduced the subsequent conversion of HMF, which would decrease the yield to the desired product. By appropriate selection of the extracting solvent and the addition of a salt or phase modifiers (DMSO and 1-methyl-2-pyrrolidinone) to the aqueous phase to improve the partitioning of HMF into the extracting phase, high selectivities to the HMF product could be achieved. For example, a 30 wt. % fructose solution saturated with NaCl using 1-butanol as the extracting solvent gave an HMF selectivity of 82%.

Conclusions

As discussed here, examples are starting to emerge on how to tailor heterogeneous catalysts and the reaction systems utilizing them for the efficient conversion of biorenewable feedstocks. However, the economic hurdle to replace fossil carbon with renewable carbon in chemical and fuel applications is quite demanding, so significant improvements in catalyst technology are needed. To achieve the necessary heterogeneous catalyst advancements, more advanced fundamental knowledge about how catalysts can be designed specifically for converting biorenewable feedstocks is critical. The unique challenges

associated with designing catalysts for this application will be a rich source of new research directions for heterogeneous catalysis.

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